

Fast convergence to equilibrium for long-chain polymer melts using a MD/continuum hybrid method

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Effective and fast convergence toward an equilibrium state for long-chain polymer melts is realized by a hybrid method coupling molecular dynamics and the elastic continuum. The required simulation time to achieve the equilibrium state is reduced drastically compared with conventional equilibration methods. The polymers move on a wide range of the energy landscape due to large-scale fluctuation generated by the elastic continuum. A variety of chain structures is generated in the polymer melt which results in the fast convergence to the equilibrium state.

I. INTRODUCTION

Atomistic simulations for polymers have been studied intensively. Especially molecular dynamics (MD) calculations for polymers in order to reveal the dynamical behavior of the chain structure have been carried out. MD calculations for long-chain polymers, however, have been limited by the massive computational costs due to the very long relaxation times of entangled long-chain polymer melts. According to reptation theory, the relaxation time of an entangled polymer melt consisting of chains with N monomers scales as N^3 . This means that a prohibitively long simulation time is needed to relax a dense polymer melt. Moreover, a complex system such as an entangled polymer melt exhibits a huge number of local-minimum energy states in the free energy surface. Energetic barriers much larger than the thermal energies separate the initial configurations from the final equilibrium states, which leads to relaxation times far greater than currently accessible computational resources allow.

The coarse-grained (CG) approach for polymer molecules, in which multiple atoms are combined into a large bead, enable us to extend the spatial and time scales of the simulation. In particular, the time scales up to several orders of magnitude from the atomistic level¹. The length of the chain polymer is, however, limited to the order of 10^4 monomers even with the CG approach².

A variety of method has been proposed for obtaining well-equilibrated CG polymer. Auhl *et al.* used the initial configuration reducing the density fluctuation and a double-pivot algorithm⁴ for a MD calculation³. They demonstrated the effectiveness of their method in long-chain polymer simulations. Gao proposed a method of polymer chain generation by connecting the polymer to monomers, combining with the relaxation of polymer conformations by MD step⁵. Perez *et al.* confirmed that the relaxation is performed while the chains are generated and showed an applicability of this method to complex polymers such as nanostructured polymer⁶. Subramanian generated the well equilibrated polymer by affinely scaling the simulation box and adding the beads along the contour of the chain, and applied it to the cyclic polymers⁷. Methods for overcoming the local energy minimum on the energy surface have been intensively studied^{8–12}. The multicanonical MD method¹³ enables sampling over a much larger phase space, and was applied to a CG model of protein folding¹⁴.

In the present paper, MD simulations for long-chain polymer melts are performed by a

hybrid MD/continuum method, in which the dynamics of the atoms is coupled with the those of the continuum degrees of freedom concurrently. This hybrid method was originally proposed by our group, and it has been applied to a simple one-dimensional system^{15,16}, in which the spring force of the continuum acts on the atomic chain system and generates large-scale fluctuations and a variety of atomic phonon modes in the atomic chain. In the present paper, the hybrid method is applied to a polymer melt consisting of long-chain polymers. We demonstrate that the large-scale fluctuation induces a large number of states of the long-chain polymers, which overcomes the energetic barriers, and leads to the fast convergence towards the final equilibrium state. Our purpose is to show the result of accelerating MD calculations using the MD/continuum hybrid method and the effectiveness of this method for long-chain polymer simulations.

II. METHOD

We describe a single polymer as a bead-spring chain in which monomers of the polymer are represented by spherical beads. The beads have an excluded volume described by the repulsive force of the 12-6 Lennard Jones potential.

$$U_{LJ}(r) = \begin{cases} 4\epsilon\{(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6 + \frac{1}{4}\} & r \leq r_c \\ 0 & r > r_c \end{cases}, \quad (1)$$

where the cutoff radius r_c is set as $2^{1/6}\sigma$. Each bead is connected with the neighboring beads in the polymer chain via a finite extensible non-linear elastic (FENE) potential as

$$U_{FENE}(r) = \begin{cases} -0.5kR_0^2 \ln(1 - (r/R_0)^2) & r \leq R_0 \\ \infty & r > R_0 \end{cases}, \quad (2)$$

where $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$. In addition, we adopt a bending potential for the polymer defined by

$$U_{bend}(\theta) = k_\theta(1 - \cos\theta), \quad (3)$$

where θ is the angle between the neighboring bonds within the polymer chain. k_θ is set to 0.25ϵ . This bending potential is applied in order to illustrate the wide range energy covered by the hybrid method as will be mentioned in discussion. The calculation is performed using the software package ESPResSo¹⁷.

The above CG polymer model is connected with the elastic continuum. Details of the MD/continuum hybrid method are explained in Ref.¹⁵, and here the procedure of the hybrid method is only briefly explained. The elastic continuum surrounds the MD cell including the CG polymer model and the elastic stress acts on the MD cell. In the case of a constant-pressure MD method¹⁸, the constant pressure acts on the MD cell. The constant pressure is replaced by the elastic stress of the continuum in the hybrid method as shown in Fig.1. Since the present system is considered to be isotropic, the cubic MD cell is under isotropic stress of the elastic continuum, which is described by the springs as shown in Fig. 1. According to the procedure of the MD/continuum hybrid method¹⁵, we can describe the Lagrangian functional L of the present hybrid model consisting of N particles in the MD cell with the volume V and the N_s springs as

$$\begin{aligned}
L(\{\mathbf{s}_i, \dot{\mathbf{s}}_i\}, V, \dot{V}, \{u_\mu, \dot{u}_\mu\}) = & \sum_{i=1}^N \frac{mV^{2/3} \dot{\mathbf{s}}_i \cdot \dot{\mathbf{s}}_i}{2} - \phi(\{\mathbf{s}_i\}, V) \\
& + \frac{Q\dot{V}^2}{2} - \frac{K}{2}(V - V_0 - u_1)^2 + \frac{M\dot{u}_1^2}{2} \\
& + \sum_{\mu=2}^{N_s} \frac{M\dot{u}_\mu^2}{2} - \frac{K(u_{\mu-1} - u_\mu)^2}{2},
\end{aligned} \tag{4}$$

where \mathbf{s}_i are the scaled coordinates of the particles, such that the Cartesian positions \mathbf{r}_i are $\mathbf{r}_i = V^{1/3}\mathbf{s}_i$. u_μ are the reduced displacements of the springs in volume units. m and M are the masses of the particles and the springs, and Q is the inertial mass for the motion of the volume V , which is also presented in the standard constant-pressure MD method¹⁸. ϕ is the potential energy between the particles of the CG polymer model. The fourth term $\frac{K}{2}(V - V_0 - u_1)^2$ corresponds to the elastic potential energy of the first spring ($\mu = 1$) as is illustrated in Fig.1(c). This energy depends on the volume V , the displacement of this spring u_1 , in which K is the spring constant. V_0 corresponds to the volume under no displacement applied on springs. The initial displacements and their velocities of the springs u_μ, \dot{u}_μ are set so as to apply the pressure on the CG model. The displacement of terminal spring u_{N_s} is fixed. The equations of the motion for the particles, volume and the springs are derived easily from the above Lagrangian.

$$m \frac{d\dot{\mathbf{s}}_i}{dt} = -V^{-2/3} \frac{\partial \phi}{\partial \mathbf{s}_i} - \frac{2}{3} \frac{\dot{V}}{V} m \dot{\mathbf{s}}_i, \tag{5}$$

$$Q \frac{d\dot{V}}{dt} = \frac{1}{3V} \sum_{i=1}^N \left(m V^{2/3} \dot{\mathbf{s}}_i^2 - \mathbf{s}_i \cdot \frac{\partial \phi}{\partial \mathbf{s}_i} \right) - K(V - V_0 - u_1), \quad (6)$$

$$M \frac{d\dot{u}_\mu}{dt} = \begin{cases} K(V - V_0 - u_\mu) - K(u_\mu - u_{\mu+1}) & , \quad (\mu = 1) \\ K(u_{\mu-1} - u_\mu) - K(u_\mu - u_{\mu+1}) & , \quad (\mu = 2, 3, \dots, N_s - 1). \end{cases} \quad (7)$$

In the equation of motion (6) for the volume V , the first two terms on the right correspond to the internal pressure of the CG polymer system, and the last term is the elastic force caused by the adjacent spring ($\mu = 1$). This equation plays a role for connecting the CG polymer system of the MD cell to the springs. The simultaneous equation of the degrees of $\{\mathbf{s}_i\}$, V and $\{u_\mu\}$ is integrated numerically and we obtain the time convolution of the coordinations of the polymer, the volume of the MD cell, and the displacement of the springs.

In our simulations, we use a CG polymer consisting of 400 beads and we place 10 such CG polymers in the MD cell. The total number of beads is thus 4000. The number density of the CG polymer liquid is set to $0.85 \sigma^{-3}$ and the temperature is set to $1.0 \epsilon/k_B$. The time unit of the calculation is $\tau = \sigma(m/\epsilon)^{1/2}$. The integration of the equation of the motion is performed using a time step 0.006τ .

To show the effectiveness of the hybrid method, we investigate the required simulation time to achieve the equilibrium state. As an initial configuration for the MD calculation, each CG polymer is set to have a long stretched chain structure. Conventional Andersen constant-pressure MD is performed using the same initial configuration in order to compare it to the result of the hybrid method.

III. RESULTS

The single-chain structure is characterized by the end-to-end distance R of a single-chain polymer. Using $k_\theta = 0.25\epsilon$ of the bending potential and the average bond length $\langle b \rangle = 0.97\sigma$, the square root of $\langle R^2 \rangle$ is derived to be $26.9 \sigma^3$.

The time convolutions of the calculated R in the present MD calculations are monitored in Fig. 2, where the result obtained by the conventional method is compared with that from the hybrid method. In the conventional MD method, considerably longer simulation time ($t \sim 1.0 \times 10^6 \tau$) is needed to obtain a stable value of R , which is in good agreement with the above analytical value. The long-chain polymer such as the present model has

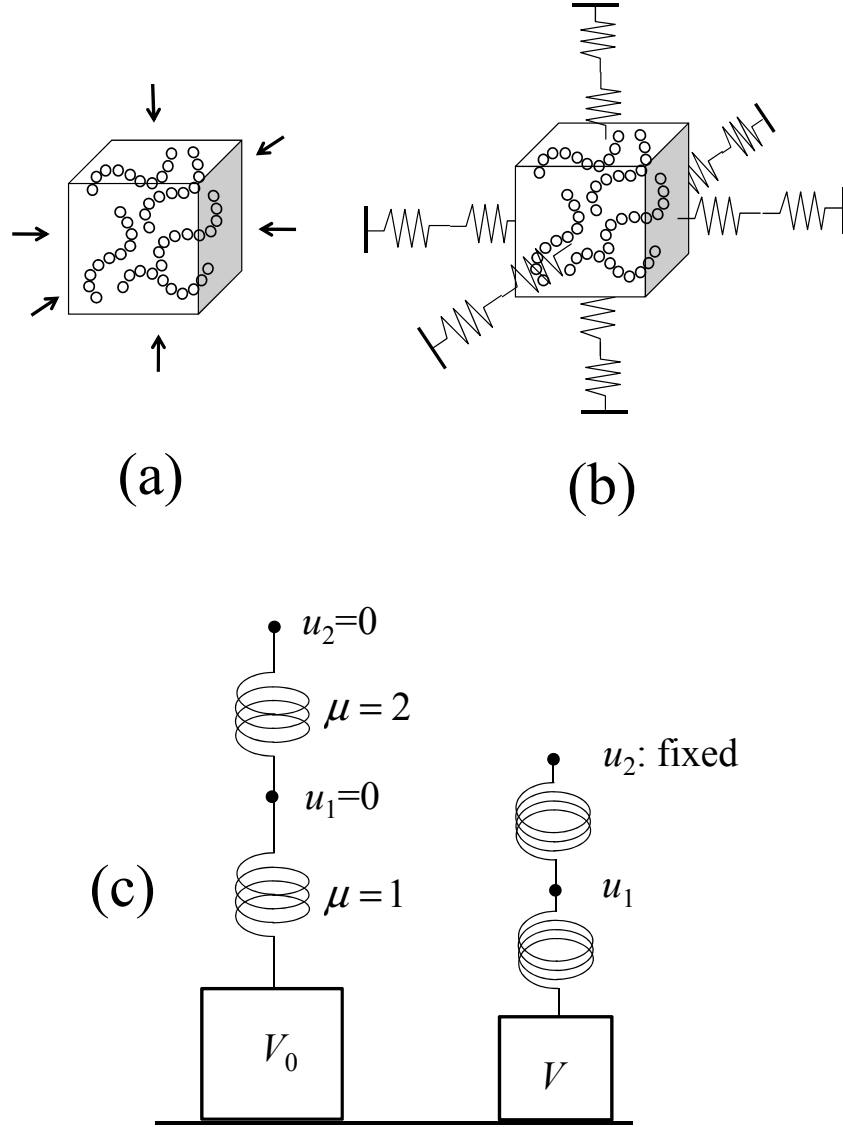


FIG. 1. Schematic views of (a) a standard constant-pressure MD model and (b)(c) the hybrid model. (a) The polymer system consists of monomers (open circle) in a cubic MD cell under an external constant pressure. (b) The springs enclose the cubic MD cell and isotropic forces by the springs act on the polymer system. (c) Schematic image of the hybrid model. On left-hand side no displacement is applied on springs, while on the right-hand, MD cell is compressed by the springs

very slow diffusion time and requires a long simulation time to reach the relaxation using a conventional MD method. In contrast, the R of the hybrid method is fluctuating wildly and rapidly converges toward the equilibrium value. After a simulation with the hybrid method

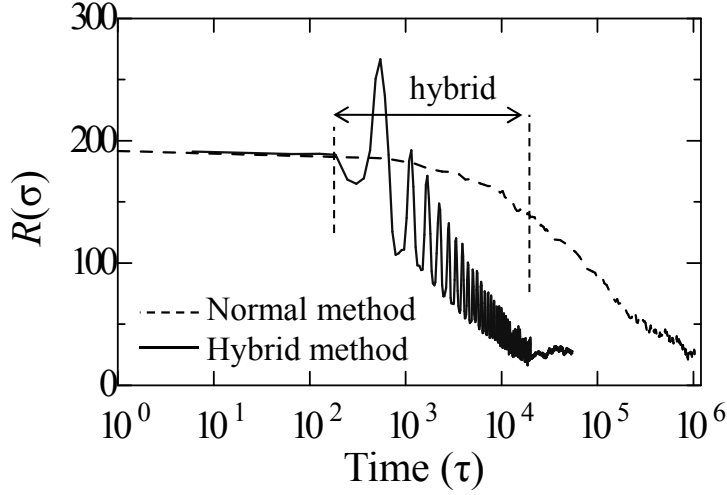


FIG. 2. Time convolutions of the end-to-end distance R of polymer melts obtained by the conventional method (broken line) and hybrid method (solid line). The calculation with the hybrid method stops at $t = 2.0 \times 10^4 \tau$, and the constant-pressure MD calculation is continued after that.

until $t = 2.0 \times 10^4 \tau$, the calculation is continued with the conventional MD method. The required time to reach the equilibrium state using the hybrid method is $t \sim 10^4 \tau$, which is about one hundredth of the time required using the conventional method.

Snapshots of a single polymer obtained by the conventional method and by the hybrid method are shown in Fig. 3. We start the MD calculations using the same initial configuration of a long stretched chain as shown in Fig. 3($t = 0$). At $t = 4.5 \times 10^4 \tau$, the polymer configuration of the conventional method still has a stretched chain structure, while that of the hybrid method has a well equilibrated, entangled, structure. In general a flexible polymer such as the present polymer model has an entangled structure in the equilibrium state. A well-equilibrated state can be obtained at $t = 4.5 \times 10^4 \tau$ by the hybrid method, while we manage to obtain the equilibrium structure only at $t \sim 10^6 \tau$ by the conventional method.

In addition, we derive the mean square internal distance $\langle R(n)^2 \rangle$, averaged over all internal distances $n = |i - j|$ along all the polymer chains, where $i < j \in [1, N]$ are the monomer indices. It is also confirmed from the time convolution of $\langle R(n)^2 \rangle$ that the MD calculation is accelerated toward equilibrium state by hybrid method. It is shown in Fig.4 that the curve of $\langle R(n)^2 \rangle / n$ obtained by the hybrid method at $t = 4.5 \times 10^4 \tau$ is

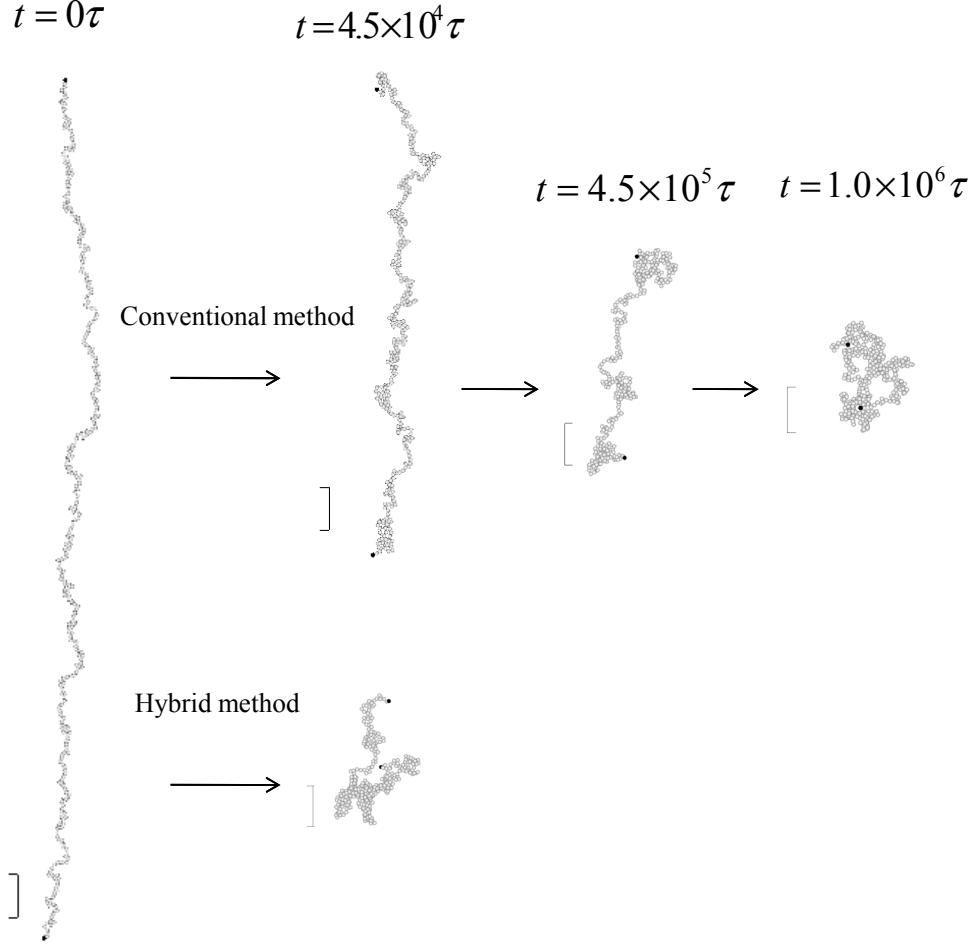


FIG. 3. Time convolution of a single polymer configuration obtained by the conventional method, compared to the hybrid method. This is one polymer chosen from ten polymers in the simulation system. Guides in figure indicate the length of 10σ .

consistent with that of the final equilibrium state. The curve obtained by the conventional method at $t = 4.5 \times 10^4 \tau$ is far from the equilibrium, and even at a simulation time of $t = 4.5 \times 10^5 \tau$, it still does not converge to the equilibrium. $\langle R(n)^2 \rangle$ for long distances ($n > 200$) have statistical errors due to the small number of polymers (10 polymer chains in the present calculation). As the n reaches chain length N , there exist less and less pairs of monomers, and larger statistical errors. These errors are enhanced by the small number of polymer chains and are thus influencing the result for large n .

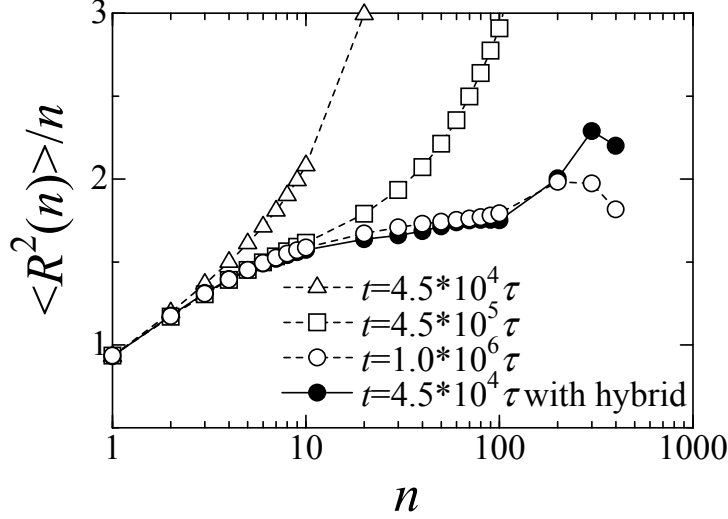


FIG. 4. Mean square internal distances obtained by the conventional method (broken lines) and hybrid method (solid line). For the conventional method, results at three different times ($t = 4.5 \times 10^4 \tau$, $4.5 \times 10^5 \tau$ and $1.0 \times 10^6 \tau$) are shown.

IV. DISCUSSION

The fluctuation of the end-to-end distance R of the hybrid model means that the chain structure of the polymer is fluctuating wildly during the simulation. The time convolution of the internal pressure of the CG polymer system and the volume of the MD cell is shown in Fig. 5. It can be seen in Fig. 5 that the internal pressure and the system volume are widely fluctuating. It can also be seen that the time convolution of the volume is out of phase with the internal pressure. These large-scale fluctuations arise in the polymer system; low pressure induces a large expansion of the volume, and a large pressure compresses the system. Hence the number density of the system is also widely fluctuating.

These large fluctuations in the polymer system are generated by the vibrations of the springs. The motion of the springs is connected with that of the MD cell as is described by Equation 6. The large-scale dynamics of the elastic continuum leads to the fluctuation of the CG polymer system and results in the fast convergence to the equilibrium. If only small stress of the elastic continuum acts on the CG polymer system, the convergence is not improved. It is confirmed in Fig. 6 that a small vibration of the springs induces small fluctuations in the polymer system, and the convergence is not improved compared to the

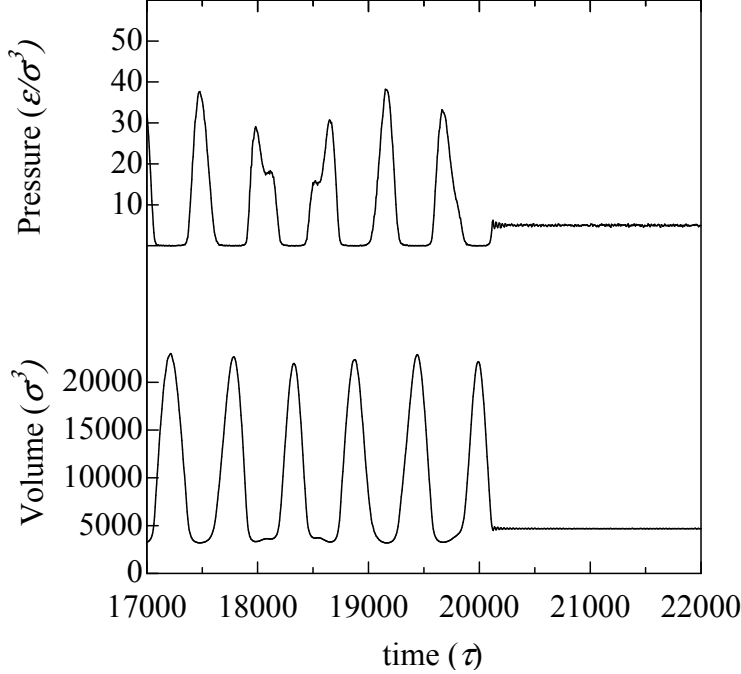


FIG. 5. Time convolution of the internal pressure and the volume of the MD cell. The calculation by the hybrid method stops at $t = 20000\tau$, and the constant-pressure MD calculation is continued after that.

conventional method in this case.

Due to the large-scale fluctuations, the trajectory of the polymer spreads over a wide phase space and a wide range of energy. The present CG polymer model has a bending potential, which is closely associated with the chain structure and its flexibility. The probability distribution function of the bending potential is shown in Fig. 7. In the conventional method, an early state ($t = 1.0 \times 10^4\tau$) is trapped in a limited local energy range around 690ϵ , which is separated from final equilibrium states of the energy around 740ϵ . In contrast, a much wider energy range is covered by the hybrid method. This suggests that the hybrid method more easily allows us to overcome energetic barriers separating the initial state from the final equilibrium state. A large variety of chain structures is generated and its trajectory is over a much wider phase space than that of the conventional method.

In our previous studies^{15,16}, a one-dimensional model was calculated by the hybrid method and the large-scale fluctuation causes the generation of a variety of phonons in the particle system. The phonons obtained by the hybrid model reproduced those by large-scale all-atom

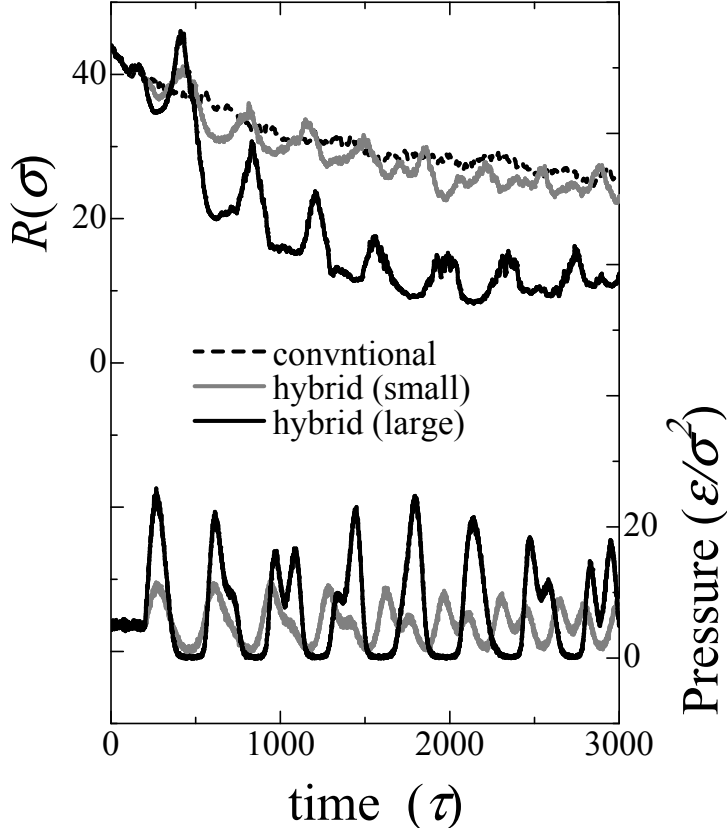


FIG. 6. Time convolution of the end-to-end distance R and the internal pressure. The results are obtained with a smaller system than in the present calculations, where a single polymer consists of 100 coarse-grain monomers. The gray line indicates the result obtained in the case of a small fluctuation by the hybrid method, while the solid line indicates the result in the case of large-scale fluctuations.

calculations. It was shown that the hybrid model enables us to extend the *spatial scale* to much larger values. In the present study, the hybrid method is applied to the long-chain polymer that has very slow diffusion dynamics. The required simulation time to reach the equilibrium state of the polymer melt is reduced drastically. The present hybrid model thus enables us to reach a much wider *time scale* than that by the conventional MD method.

Although the present model is simple, the hybrid method can be applied to more realistic and complex systems such as polycarbonate¹⁹ and protein molecules. The equilibrium structure and various properties at finite temperatures can be obtained with reasonable computational cost.

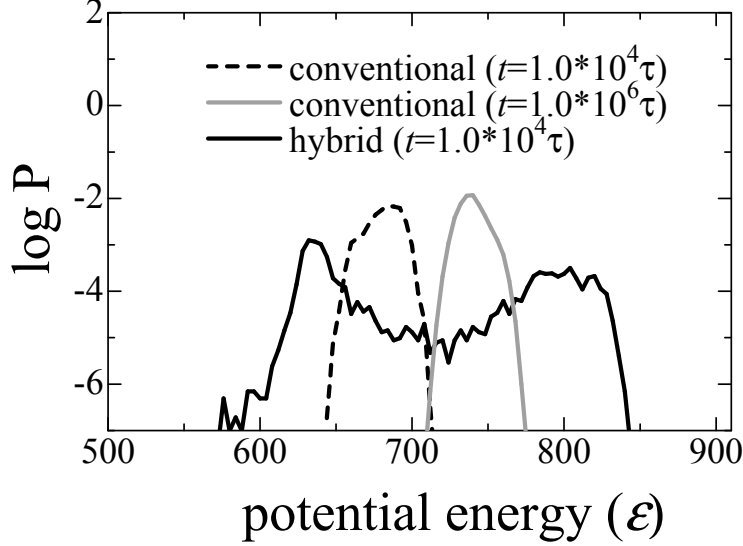


FIG. 7. The probability distribution functions of the bending potential for the hybrid method together with the conventional method.

V. CONCLUSION

We couple a CG polymer model and an elastic continuum using the hybrid method. The polymer melt consisting of the CG polymers is simulated and it is shown that fast convergence towards the equilibrium state of the polymer melt is achieved. The elastic continuum of the hybrid model acts on the polymer system and produces large scale fluctuations. The fluctuations allow the polymer system to sample over a much wider phase space than the conventional method, inducing a variety of polymer states, and leads to fast convergence toward the equilibrium.

VI. ACKNOWLEDGEMENTS

We thank Dr Karen Johnston for helpful discussion and fruitful collaboration. This work was supported by Functional Materials Programme of Tekes, Finland, and by a Grant-in-Aid for Scientific Research in Priority Areas (no.17064012) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We also thank Japan Aerospace Exploration Agency (JAXA) for allowing us to use JAXA supercomputer system.

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